Oxygen Reduction Reaction on Pt and Pt Bimetallic Surfaces

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In this paper we present recent progress in the development of the oxygen reduction reaction (ORR) catalysis on well-defined surfaces. The focus is on two type of metallic surfaces: platinum single crystals and bimetallic surfaces based on platinum. The single crystal results provide insight into the effects of the platinum structure on the kinetics of the ORR, and create a fundamental link between the specific activity of Pt (rate per unit area) and particle size (for various particle shapes). The results show that the structure sensitive kinetics of the ORR arise primarily due to structure sensitive adsorption of anions.

All measurements were carried out by making use of the rotating ring-disk electrode (RRDE) technique. The Pt single crystals and polycrystalline Pt_3M alloy (M = Ni, Co) electrodes were prepared either by the flame annealing technique or in ultra-high vacuum by sputtering/annealing cycles, respectively. After preparation, the electrodes were transferred into the disk position of an insertable ring-disk arbor. Before the transfer, the Pt_3M alloys were characterized in UHV by Auger electron spectroscopy (AES) and Low Energy Ion Scattering (LEIS). LEIS revealed that the surface composition of the Pt_3M alloy electrodes equaled the bulk composition, *i.e.*, the surface consists of 75 % Pt and 25 % of the alloying component.

For measurements with the high-surface area catalysts, we used the thin-film RDE method. We investigated a commercially available Pt catalyst (20 wt% platinum supported on Vulcan XC72), two Pt-Co-alloy catalysts (20 wt% PtCo/Vulcan XC72, a/o = 1/1, and 20 wt% Pt_3Co/Vulcan XC72, a/o = 3/1), and a Pt_3Ni/Vulcan XC72 (20 wt%, a/o = 3/1) catalyst (E-Tek). All potentials in this manuscript refer to that of the reversible hydrogen electrode.

The ORR on Pt(hkl)-Cl_{ad} electrodes is strongly inhibited. The single crystal results showed that Cl_{ad} has two effects in the kinetics of the: (i) Cl_{ad} acts as a site-blocking species which is reducing the number of active sites for the adsorption of O_2 molecules and (ii) Cl_{ad} is affecting the number of sites required for the breaking of the O-O bond. The same physical model of action was used to explain the effect of Cl^- on the rate of the ORR on supported Pt catalysts.

Several investigations have been carried out on supported catalyst to determine the role of alloying in the electrocatalytic activity of Pt for the ORR. A definitive determination, however, remains elusive. The knowledge of the electrocatalysis of the ORR on model bimetallic surfaces on Pt-Ni and Pt-Co bulk alloys was used to resolve the enhanced ORR kinetics on supported Pt-Ni and Pt-Co catalysts. We found significant improvement of the ORR catalyses on Pt based alloy systems will require the inhibition of Pt-OH formation beyond 0.8 V.